

# Derivation of time-dependent transition probability for $2e - 2h$ generation from $1e - 1h$ state in the presence of external electromagnetic field

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In this work, we investigate the effect of electromagnetic (EM) field on the generation of  $2e-2h$  states from  $1e-2h$  states. One of the fundamental ways by which electromagnetic (EM) waves interact with matter is by the generation of excited electronic states. The interaction of EM field with atoms and molecules is given by the field-dependent Hamiltonian. Excited states are intrinsically transient in nature because they are not stationary states of the field-dependent Hamiltonian. Consequently, the time-dependent dynamics of excited states depend strongly on the external electromagnetic field. Starting with the  $1e-1h$  excitation in a general many-electron system, the system was propagated in time using time-dependent perturbation theory (TDPT). The expression for time-dependent transition probability of  $(1e - 1h) \rightarrow (2e - 2h)$  was evaluated for a given time  $t$  up to second-order in TDPT using diagrammatic techniques. The derivation does not assume any *a priori* approximations to the electron-electron correlation operator and presents the derivation of a complete set of contributing diagrams associated with the full configuration interaction wave function. The result from this work show that the calculation of time-dependent transition probability can be factored into a time-independent and time-dependent components. This is a significant outcome for efficient computation of the time-dependent transition probability because it allows for pre-computation of time-independent components before the start of the calculations.

Keywords: (PhySH) Single-photon ionization & excitation, Biexcitons, Perturbation theory, Renormalization

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## I. INTRODUCTION

In 1961, Shockley and Queisser found the upper theoretical limit for the efficiency of p-n junction solar energy converters to be about 30%. This is known as the Shockley-Queisser thermodynamic limit.[1] Since then, there have been two main approaches for increasing the efficiency of the solar cell by means of producing multiple photogenerated excitons from a single absorbed photon. The two approaches are multiple exciton generation (MEG) (carrier multiplication (CM)) and singlet fission (SF).

In MEG, the exciton multiplication occurs when the absorbed photon is at least twice the nanocrystal band gap. This has been tested experimentally in semiconductor nanocrystals,[2–6] quantum dots,[7–10] quantum wires, and quantum rods.[11, 12] The affect of size, shape, and composition of PbS, PbSe, PbTe nanocrystals has on MEG was studied by Padilha et. al.[13] MEG also has been shown to occur in carbon nanotubes[14] as well as graphene.[15] The generation of multiexcitons has been subject of intense theoretical research.[16] For example, symmetry-adapted configuration interaction method has been used to study the excited states of nanocrystals, such as lead selenide and silicon quantum dots, to determine the energetic threshold of MEG.[17, 18] In addition to energetics requirements, the importance of electron-phonon coupling for multiexciton generation and multiexciton recombination (MER) in semiconductor quantum dots has also been demonstrated.[19]

The second avenue to generate multiple excitons is singlet fission. In molecular chromophores that have a triplet state energy that is close to 1/2 the energy of the first allowed optical transition ( $S_1-S_0$ ), exciton multiplication can occur upon photoexcitation to produce two triplet states from the single singlet state.[20, 21] Johnson et. al. showed this using 1,3-Diphenylisobenzofuran as a model chromophore.[22] Thompson et. al. shows the magnetic field dependence of singlet fission in solutions of diphenyl tetracene.[23] Wu et. al. presents that tetracene is the best candidate in silicon solar cells to increase efficiency using SF. They report a quantum efficiency of  $127\% \pm 18\%$ . [24]

In this work, we present a theoretical study of the effect of an external electromagnetic field on the generation of a biexcitonic state from a single excitonic state. The main goal of this work is to present a systematic derivation of the time-dependent transition probability for the  $(1e - 1h) \rightarrow (2e - 2h)$  process. We consider a general many-electron system in the presence of an external EM field. The system is assumed to be excited at  $t = 0$  and the is propagated in time using field-dependent Hamiltonian. The form of the field-dependent Hamiltonian and the initial conditions are described in section II. The time-propagation of the state vector is performed using time-ordered field-dependent propagator (section III) using time-dependent perturbation theory and the 0th, 1st and 2nd order contributions to the time-dependent transition amplitudes were derived in terms for second-quantized operators(section IV). The transition amplitudes were expressed in terms of the time-independent Hugenholtz diagrams[25] (section V) with time-dependent vertex amplitudes. Finally, simplified expressions for calculating time-dependent vertex amplitudes that is amenable to computer implementation were derived (section VI). The key results and conclusions from the derivation are summarized in section VII.

## II. SYSTEM INFORMATION AND DEFINITION

We define the reference effective one-particle Hamiltonian as,

$$h_0 = \frac{-\hbar^2}{2m} \nabla^2 + v_{\text{ext}} + v_{\text{eff}} \quad (1)$$

where  $v_{\text{eff}}$  is the effective one-particle operator and can be approximated using  $v_{\text{HF}}, v_{\text{KS}}, v_{\text{ps}}$ , or  $v_{\text{model}}$ . The eigen-spectrum of the  $h_0$  is used for the construction of the creation and annihilation operators

$$h_0 \chi_p = \epsilon_p \chi_p. \quad (2)$$

The N-electron non-interacting Hamiltonian is defined as,

$$H_0 = \sum_i^N h(i). \quad (3)$$

The ground state of  $H_0$  is defined as the quasiparticle vacuum,

$$|0\rangle \equiv \Phi_0. \quad (4)$$

The Hamiltonian for the interacting N-electron system is defined as,

$$H = H_0 + W \quad (5)$$

where  $W$  is the residual electron-electron interaction not included in the one-body operator  $v_{\text{eff}}$

$$W = \sum_{i < j}^N r_{ij}^{-1} - \sum_i^N v_{\text{eff}}(i). \quad (6)$$

The non-interacting electron-hole wave function is defined using the creation operators for quasi-electrons and quasi-holes

$$|\Phi_i^a\rangle = \{a^\dagger i\}|0\rangle. \quad (7)$$

The correlated electron-hole wave function is defined using a correlation operator,  $\Omega_n$ ,

$$|\Psi\rangle = \Omega_n |\Phi_i^a\rangle \quad (8)$$

where  $\Omega_n$  will be defined later.

We are interested in the time-development of the correlated wave function under the influence of an external electromagnetic field. The interaction between the molecule and the EM field is given by the time-dependent interaction operator  $V_F(t)$ .<sup>[26]</sup> The total field dependent Hamiltonian is defined as,

$$H_F(t) = H_0 + V_F(t). \quad (9)$$

### III. METHOD FOR TIME-PROPAGATION

In this work, we will work in the Dirac's interaction representation. In this representation, the total interaction potential is defined using the following similarity-transformation,

$$Z_I^F(t) = e^{+iH_0 t/\hbar} [V_F(t) + W] e^{-iH_0 t/\hbar}. \quad (10)$$

The field-dependent time-development operator,  $U_F(t, 0)$ , is defined as,

$$U_F(t, 0) = 1 + \sum_{n=1} U_F^{(n)}(t) \quad (11)$$

where  $U_F^{(n)}(t)$  is defined as,

$$U_F^{(n)}(t) = C_n \int_0^t dt_1 dt_2 \dots dt_n \mathcal{T}[Z_I^F(t_1) Z_I^F(t_2) \dots Z_I^F(t_n)]. \quad (12)$$

We assume that the system at  $t = 0$  is described by the state vector  $\Psi(0) = \Omega_n |\Phi_i^a\rangle$ . The time-development of this state vector to time  $t$  is given by the following expression,

$$|\Psi_F(t)\rangle = U_F(t, 0) |\Psi(0)\rangle. \quad (13)$$

The subscript  $F$  in the above equation implies that the time-development was performed under the influence of the external field,  $V_F$ . In this work, we are interested in the 2e-2h generation from 1e-1h excitation.

$$(\text{Carrier multiplication}) P_{F, X \rightarrow X_2}(t) = |\langle 0 | \{k^\dagger j^\dagger bc\} | \Psi_F(t) \rangle|^2. \quad (14)$$

For the purpose of this derivation, it is useful to write the transition probability in terms of the transition amplitude  $I$  as shown below,

$$P_{F, X \rightarrow X_2}(t_f) = \int_0^{t_f} dt [I_F(t)] [I_F(t)]^* \quad (15)$$

where,

$$I_F(t) = \langle 0 | \{k^\dagger j^\dagger bc\} | \Psi_F(t) \rangle. \quad (16)$$

In this work, we will use both Wick's contraction and diagrammatic methods for deriving the expression for the time-dependent transition amplitudes. The first step in this many-step derivation is to write all the relevant quantities as vacuum expectation values. Writing the expression in terms of time-development operator,

$$I_F(t) = \langle 0 | \{k^\dagger j^\dagger bc\} U_F(t, 0) \Omega_X \{a^\dagger i\} | 0 \rangle. \quad (17)$$

For the  $n$ th-order term in the time-development operator, we define

$$I_F^{(n)}(t_1, t_2, \dots, t_n) = \langle 0 | \{k^\dagger j^\dagger bc\} \mathcal{T}[Z_I^F(t_1) Z_I^F(t_2) \dots Z_I^F(t_n)] \Omega_X \{a^\dagger i\} | 0 \rangle. \quad (18)$$

Using Wick's theorem, we conclude the only fully contracted terms will have non-zero contribution to the above expression

$$I_F^{(n)}(t_1, t_2, \dots, t_n) = \langle 0 | \{k^\dagger j^\dagger bc\} \mathcal{T}[Z_I^F(t_1) Z_I^F(t_2) \dots Z_I^F(t_n)] \Omega_X \{a^\dagger i\} | 0 \rangle_C. \quad (19)$$

In this work, we evaluate the above expansion up to second-order using diagrammatic techniques. The explicit expression for  $I_F^{(0)}$ ,  $I_F^{(1)}$  and  $I_F^{(2)}$  are presented in Sec. [IV A](#), [IV B](#), and [IV C](#).

## IV. PERTURBATIVE TREATMENT OF TRANSITION AMPLITUDES

### A. 0th order contribution

The zeroth order term is field-independent and is given by the expression,

$$I_F^{(0)} = \langle 0 | \{k j^\dagger bc\} \Omega_X \{a^\dagger i\} | 0 \rangle_C. \quad (20)$$

As expected, the above expression is independent of time. The Wick's contraction required to evaluate this term is denoted by the following expression,

$$\eta^{(3a)} = \langle 0 | \{k j^\dagger bc\} \Omega_X \{a^\dagger i\} | 0 \rangle_L. \quad (21)$$

We note that only connected diagrams contribute to the above expression and this fact is denoted by subscript "L".

### B. 1st order contribution

The first-order term is:

$$I_F^{(1)}(t_1) = \langle 0 | \{k j^\dagger bc\} Z_I^F(t_1) \Omega_X \{a^\dagger i\} | 0 \rangle_C. \quad (22)$$

To evaluate the above expression, we will have to derive the expression of the time-dependent interaction potential,  $Z_I^F(t_1)$ , which is defined as,

$$Z_I^F(t) = e^{+iH_0 t/\hbar} [V_F(t) + W] e^{-iH_0 t/\hbar}. \quad (23)$$

In this derivation, we will split the above expression into 1-body and 2-body terms,

$$V_I^F(t) = e^{+iH_0 t/\hbar} V_F(t) e^{-iH_0 t/\hbar} \quad (24)$$

$$W_I^F(t) = e^{+iH_0 t/\hbar} W e^{-iH_0 t/\hbar}. \quad (25)$$

The 1-body and 2-body time-dependent operators are represented using time-dependent amplitudes,

$$V_I^F(t) = \sum_{pq} A_{pq}(t) p^\dagger q \quad (26)$$

$$= \sum_{pq} A_{pq}(t) \{p^\dagger q\} + \langle 0 | V_I^F(t) | 0 \rangle \quad (27)$$

$$= \sum_{pq} A_{pq}(t) \{p^\dagger q\} + \langle 0 | V_F(t) | 0 \rangle. \quad (28)$$

Similarly the 2-body term is given as,

$$W_I^F(t) = \frac{1}{2} \sum_{pqrs} B_{pqrs}(t) p^\dagger q^\dagger sr \quad (29)$$

$$= \frac{1}{2} \sum_{pqrs} B_{pqrs}(t) \{p^\dagger q^\dagger sr\} + \sum_{pq} C_{pq}(t) \{p^\dagger q\} + \langle 0 | W_I^F(t) | 0 \rangle \quad (30)$$

where,

$$C_{pq}(t) = \sum_i^N B_{piqi}(t) - B_{ptiq}(t). \quad (31)$$

Adding the terms and rewriting them in terms of normal-ordered 2-body, 1-body, and vacuum expectation value terms we get,

$$Z_I^F(t) = \frac{1}{2} \sum_{pqrs} B_{pqrs}(t) \{p^\dagger q^\dagger sr\} + \sum_{pq} D_{pq}(t) \{p^\dagger q\} + \langle 0 | Z_I^F(t) | 0 \rangle. \quad (32)$$

where,

$$\mathbf{D}(t) = \mathbf{A}(t) + \mathbf{C}(t) \quad (33)$$

$$Z_I^F(t) = Z_0(t) + Z_D(t) + Z_B(t). \quad (34)$$

The 1st order probability for generation of 2e-2h from 1e-1h is given by the following expression,

$$I_F^{(1)}(t) = \langle 0 | \{k j^\dagger bc\} [Z_0 + Z_D + Z_B] \Omega_X \{a^\dagger i\} | 0 \rangle_C. \quad (35)$$

Summing over

$$I_F^{(1)}(t) = Z_0(t) I^{(0)} + \sum_{pq} D_{pq}(t) \eta_{pq}^{(4a)} + \sum_{pqrs} B_{pqrs}(t) \eta_{pqrs}^{(4b)} \quad (36)$$

where,

$$\eta_{pq}^{(4a)} = \langle 0 | \{k j^\dagger bc\} \{p^\dagger q\} \Omega_X \{a^\dagger i\} | 0 \rangle_C \quad (37)$$

$$\eta_{pqrs}^{(4b)} = \langle 0 | \{k j^\dagger bc\} \{p^\dagger q^\dagger sr\} \Omega_X \{a^\dagger i\} | 0 \rangle_C. \quad (38)$$

### C. 2nd order contribution

The second-order term for ( $t_1 > t_2$ ) is:

$$I_F^{(2)}(t) = \langle 0 | \{k j^\dagger bc\} Z_I^F(t_1) Z_I^F(t_2) \Omega_X \{a^\dagger i\} | 0 \rangle_C. \quad (39)$$

Substituting,

$$Z_I^F(t_1) Z_I^F(t_2) = [Z_0(t_1) + Z_D(t_1) + Z_B(t_1)] [Z_0(t_2) + Z_D(t_2) + Z_B(t_2)] \quad (40)$$

$$\begin{aligned} &= Z_0(t_1) [Z_0(t_2) + Z_D(t_2) + Z_B(t_2)] \\ &+ Z_D(t_1) [Z_0(t_2) + Z_D(t_2) + Z_B(t_2)] \\ &+ Z_B(t_1) [Z_0(t_2) + Z_D(t_2) + Z_B(t_2)] \\ &= Z_0(t_1) [Z_0(t_2) + Z_D(t_2) + Z_B(t_2)] \\ &+ [Z_D(t_1) + Z_B(t_1)] Z_0(t_2) \end{aligned} \quad (41)$$

$$\begin{aligned}
& + [Z_D(t_1)Z_B(t_2)] + [Z_B(t_1)Z_D(t_2)] \\
& + [Z_D(t_1)Z_D(t_2)] + [Z_B(t_1)Z_B(t_2)].
\end{aligned} \tag{42}$$

Adding and subtracting  $Z_0(t_1)Z_0(t_2)$  in the following expression,

$$[Z_D(t_1) + Z_B(t_1)]Z_0(t_2) = [Z_0(t_1) + Z_D(t_1) + Z_B(t_1)]Z_0(t_2) - Z_0(t_1)Z_0(t_2). \tag{43}$$

Therefore,

$$\begin{aligned}
Z_I^F(t_1)Z_I^F(t_2) &= Z_0(t_1)[Z_0(t_2) + Z_D(t_2) + Z_B(t_2)] \\
&+ [Z_0(t_1) + Z_D(t_1) + Z_B(t_1)]Z_0(t_2) \\
&+ [Z_D(t_1)Z_B(t_2)] + [Z_B(t_1)Z_D(t_2)] \\
&+ [Z_D(t_1)Z_D(t_2)] + [Z_B(t_1)Z_B(t_2)] - [Z_0(t_1)Z_0(t_2)].
\end{aligned} \tag{44}$$

We define time-reversed anti-commutation as,

$$[A(t_1), B(t_2)]_+^t = A(t_1)B(t_2) + B(t_1)A(t_2). \tag{45}$$

Using the above equation, the expression for  $I_F^{(2)}(t)$  is given as,

$$\begin{aligned}
I_F^{(2)}(t_1 t_2) &= Z_0(t_1)I_F^{(1)}(t_2) + I_F^{(1)}(t_1)Z_0(t_2) - Z_0(t_1)Z_0(t_2)I^{(0)} \\
&+ \langle 0|\{kj^\dagger bc\}[Z_D(t_1), Z_B(t_2)]_+^t \Omega_X\{a^\dagger i\}|0\rangle \\
&+ \langle 0|\{kj^\dagger bc\}[Z_D(t_1)Z_D(t_2)]\Omega_X\{a^\dagger i\}|0\rangle \\
&+ \langle 0|\{kj^\dagger bc\}[Z_B(t_1)Z_B(t_2)]\Omega_X\{a^\dagger i\}|0\rangle.
\end{aligned} \tag{46}$$

The evaluation of the terms in Eq. 46 are given by,

$$\langle 0|\{kj^\dagger bc\}[Z_D(t_1)Z_D(t_2)]\Omega_X\{a^\dagger i\}|0\rangle = \sum_{pq} \sum_{rs} D_{pq}(t_1)D_{rs}(t_2)\eta_{pqrs}^{(5a)} \tag{47}$$

$$\langle 0|\{kj^\dagger bc\}[Z_D(t_1), Z_B(t_2)]_+^t \Omega_X\{a^\dagger i\}|0\rangle = \sum_{pqrs} \sum_{xy} G_{pqrsxy}(t_1, t_2)\eta_{pqrsxy}^{(5b)} \tag{48}$$

$$\langle 0|\{kj^\dagger bc\}[Z_B(t_1)Z_B(t_2)]\Omega_X\{a^\dagger i\}|0\rangle = \sum_{pqrs} \sum_{tuvw} B_{pqrs}(t_1)B_{tuvw}(t_2)\eta_{pqrstuvw}^{(5c)} \tag{49}$$

where the time-independent components are given as,

$$\eta_{pqrs}^{(5a)} = \langle 0|\{kj^\dagger bc\}\{p^\dagger q\}\{r^\dagger s\}\Omega_X\{a^\dagger i\}|0\rangle_C \tag{50}$$

$$\eta_{pqrsxy}^{(5b)} = \langle 0|\{kj^\dagger bc\}\{p^\dagger q^\dagger sr\}\{x^\dagger y\}\Omega_X\{a^\dagger i\}|0\rangle_C \tag{51}$$

$$\eta_{pqrstuvw}^{(5c)} = \langle 0|\{kj^\dagger bc\}\{p^\dagger q^\dagger sr\}\{t^\dagger u^\dagger vw\}\Omega_X\{a^\dagger i\}|0\rangle_C \tag{52}$$

and

$$G_{pqrsxy}(t_1, t_2) = B_{pqrs}(t_1)D_{xy}(t_2) + D_{xy}(t_1)B_{pqrs}(t_2). \tag{53}$$

$$\begin{aligned}
I_F^{(2)}(t_1 t_2) &= Z_0(t_1)I_F^{(1)}(t_2) + I_F^{(1)}(t_1)Z_0(t_2) - Z_0(t_1)Z_0(t_2)I^{(0)} \\
&+ \sum_{pqrs} D_{pq}(t_1)D_{rs}(t_2)\eta_{pqrs}^{(5a)} + \sum_{pqrsxy} G_{pqrsxy}(t_1, t_2)\eta_{pqrsxy}^{(5b)} + \sum_{pqrstuvw} B_{pqrs}(t_1)B_{tuvw}(t_2)\eta_{pqrstuvw}^{(5c)}.
\end{aligned} \tag{54}$$

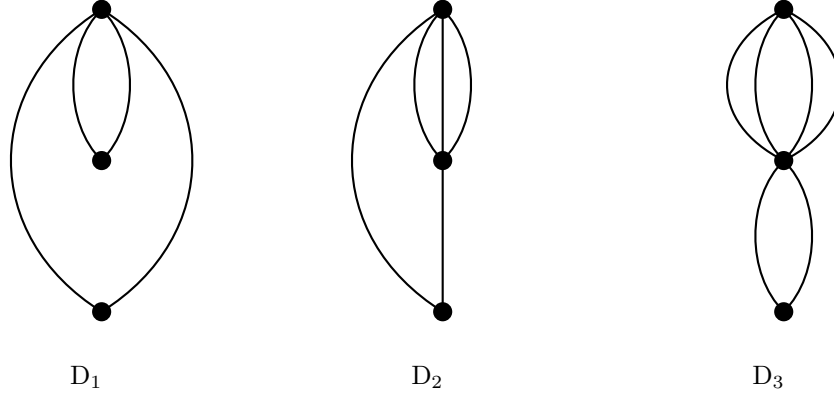


FIG. 1. 3-vertex diagrams.

## V. DIAGRAMMATIC EVALUATION OF WICK'S CONTRACTION

In this section, we derive the expressions for the  $\eta$  terms that are needed to evaluate the expression. The 3-vertex terms  $\eta^{(3a)}$  are given by the set of diagrams presented in Figure 1. We note that only linked-diagrams have non-zero contribution to  $\eta^{(3a)}$ . The expression for  $\eta^{(4)}$  can be expressed as a sum of both linked and unlinked diagrams. However, it can be shown that all unlinked diagrams have zero contribution. Analysis of the unlinked diagrams reveal that the unlinked diagrams contain the following expressions,

$$\langle 0 | \{k^\dagger j^\dagger bc\} \{a^\dagger i\} | 0 \rangle \langle 0 | Z_{D,B} \Omega | 0 \rangle = 0. \quad (55)$$

The set of linked diagrams for  $\eta^{(4a)}$  and  $\eta^{(4b)}$  are presented in Fig. 2 and Fig. 3.

The evaluation of the  $\eta^{(5)}$  expressions require both linked and unlinked diagrams. In many cases, the unlinked 5-vertex diagrams can be expressed in terms of the 3-vertex and 4-vertex diagrams derived earlier. In case of  $\eta^{(5a)}$ , this diagrammatic factorization is expressed as,

$$\eta_{pqrs}^{(5a)} = \eta_{pqrs}^{(2a)} \eta^{(3a)} + \eta_{pqrs}^{(5aL)} \quad (56)$$

where  $\eta^{(2a)}$  is the vacuum bubble

$$\eta_{pqrs}^{(2a)} = \langle 0 | \{p^\dagger q\} \{r^\dagger s\} | 0 \rangle \quad (57)$$

and  $\eta_{pqrs}^{(5aL)}$  are set of all linked diagrams and the superscript  $L$  is used to represent it. Using Wick's theorem,

$$\{p^\dagger q\} \{r^\dagger s\} = \{p^\dagger q r^\dagger s\} + \delta_{qr} \{p^\dagger s\} - \delta_{ps} \{r^\dagger q\} + \delta_{ps} \delta_{qr}. \quad (58)$$

Therefore,

$$\eta_{pqrs}^{(5aL)} = \eta_{pqrs}^{(4b)} + \delta_{qr} \eta_{ps}^{(4a)} - \delta_{ps} \eta_{rq}^{(4a)} + \delta_{ps} \delta_{qr} \eta^{(3a)}. \quad (59)$$

Similarly, the diagrams associated with  $\eta^{(5b)}$  can be factored as,

$$\eta_{pqrsxy}^{(5b)} = \eta_{xy}^{(1a)} \eta_{pqrs}^{(4b)} + \eta_{pqrs}^{(1b)} \eta_{xy}^{(4a)} + \eta_{xy}^{(1a)} \eta_{pqrs}^{(1b)} \eta^{(3a)} + \eta_{pqrsxy}^{(5bL)} \quad (60)$$

$$\eta_{pqrstuvw}^{(5c)} = \eta_{tuvw}^{(1b)} \eta_{pqrs}^{(4b)} + \eta_{pqrs}^{(1b)} \eta_{tuvw}^{(4b)} + \eta_{pqrs}^{(1b)} \eta_{tuvw}^{(1b)} \eta^{(3a)} + \eta_{pqrstuvw}^{(5cL)} \quad (61)$$

where,

$$\eta_{pq}^{(1a)} = \langle 0 | \{p^\dagger q\} | 0 \rangle \quad (62)$$

$$\eta_{pqrs}^{(1a)} = \langle 0 | \{p^\dagger q^\dagger sr\} | 0 \rangle. \quad (63)$$

In this work, we introduce a renormalization scheme where all linked 5-vertex diagrams are represented as 1-loop and 2-loop renormalized 3-vertex and 4-vertex diagrams. Using this approach, diagrams associated with  $\eta_{pqrs}^{(5aL)}$  and  $\eta_{pqrs}^{(5bL)}$  are presented in Fig. 4 and Fig. 5, respectively.

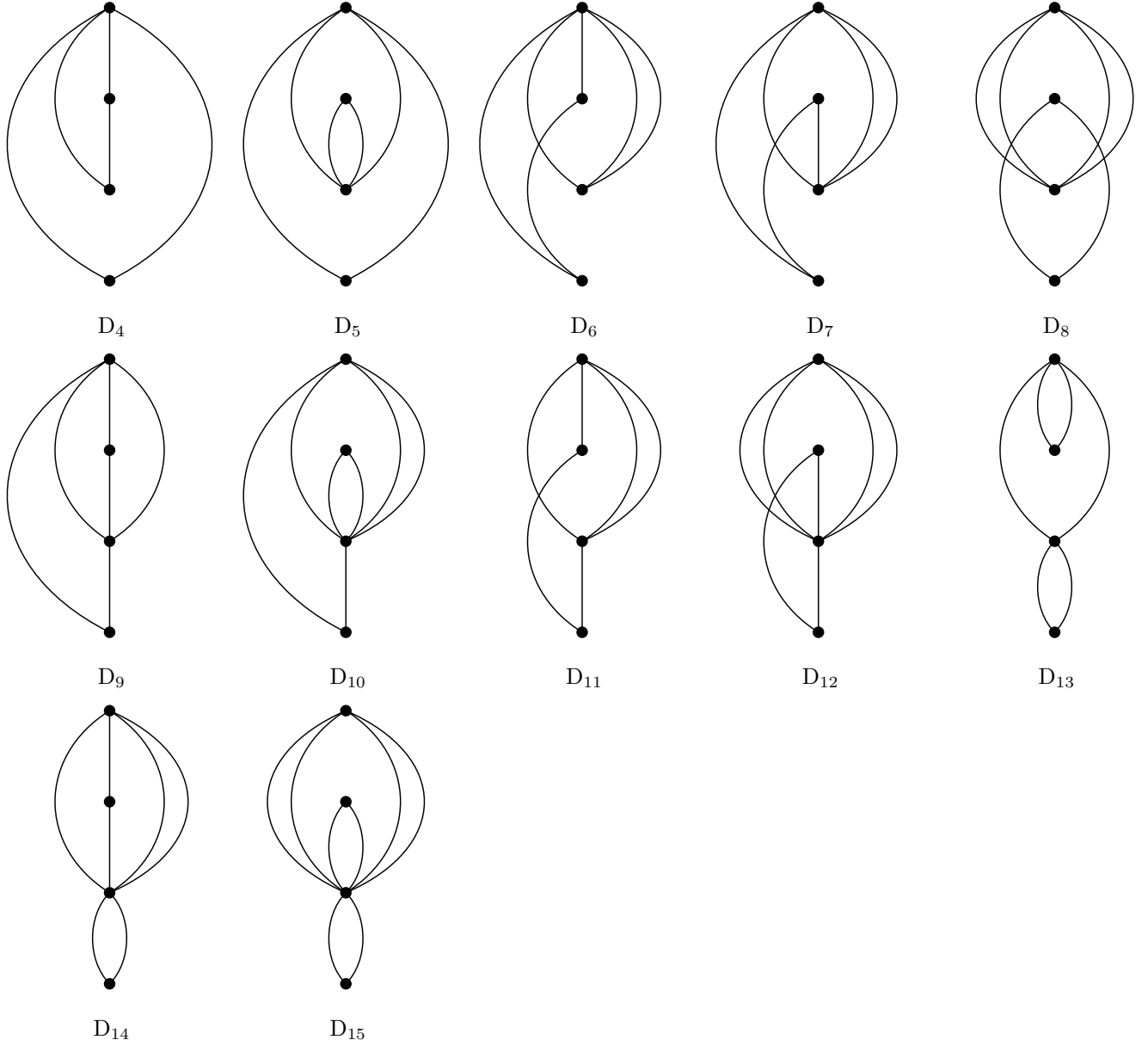


FIG. 2. Part A: 4-vertex diagrams.

## VI. EVALUATION OF TIME-DEPENDENT VERTEX AMPLITUDES

### A. Evaluation of time-dependent amplitudes associated with bare 1-body vertex

In this section, we will evaluate the expression of the time-dependent amplitude  $A_{pq}(t)$  associated with the bare 1-body vertex. The equation that defines this amplitude is given by the following equation,

$$e^{+iH_0t/\hbar} V_F(t) e^{-iH_0t/\hbar} = \sum_{pq} A_{pq}(t) p^\dagger q. \quad (64)$$

We will start by writing the second-quantized (SQ) representation of the  $V_F(t)$  operator

$$V_F(t) = \sum_{pq} v_{pq}^F(t) p^\dagger q. \quad (65)$$



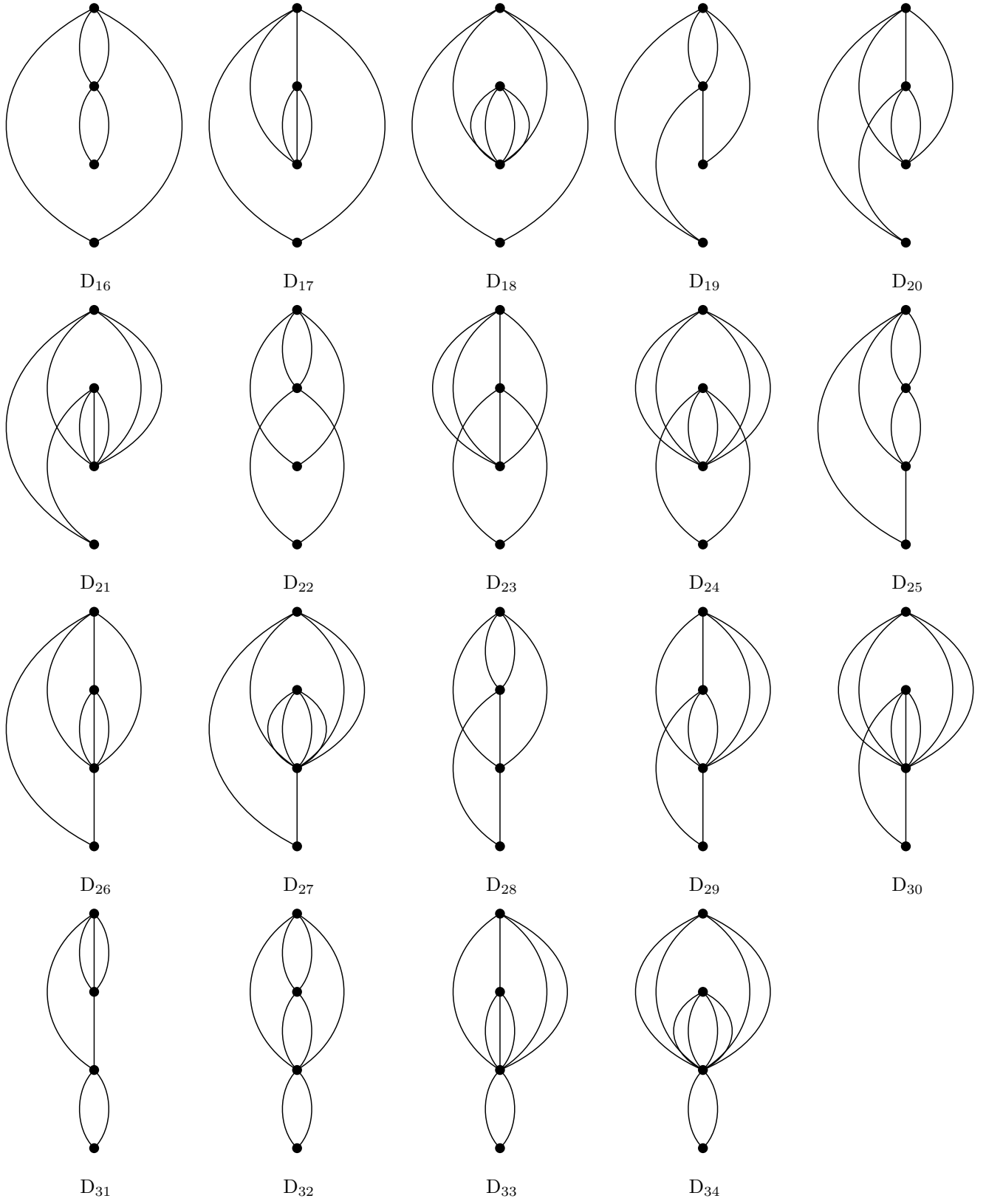


FIG. 3. Part B: 4-vertex diagrams.

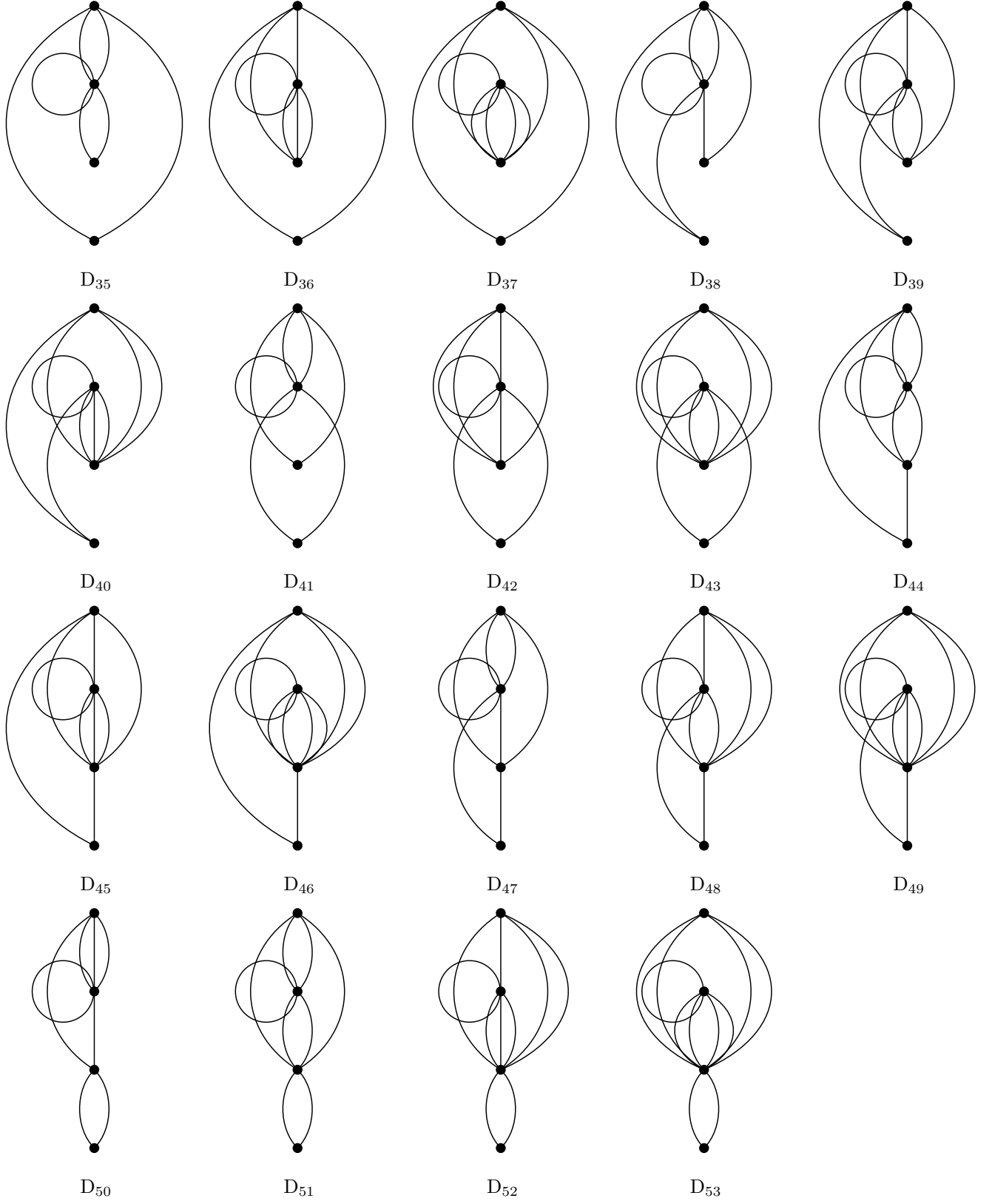


FIG. 4. 1-loop renormalized 4-vertex diagrams.

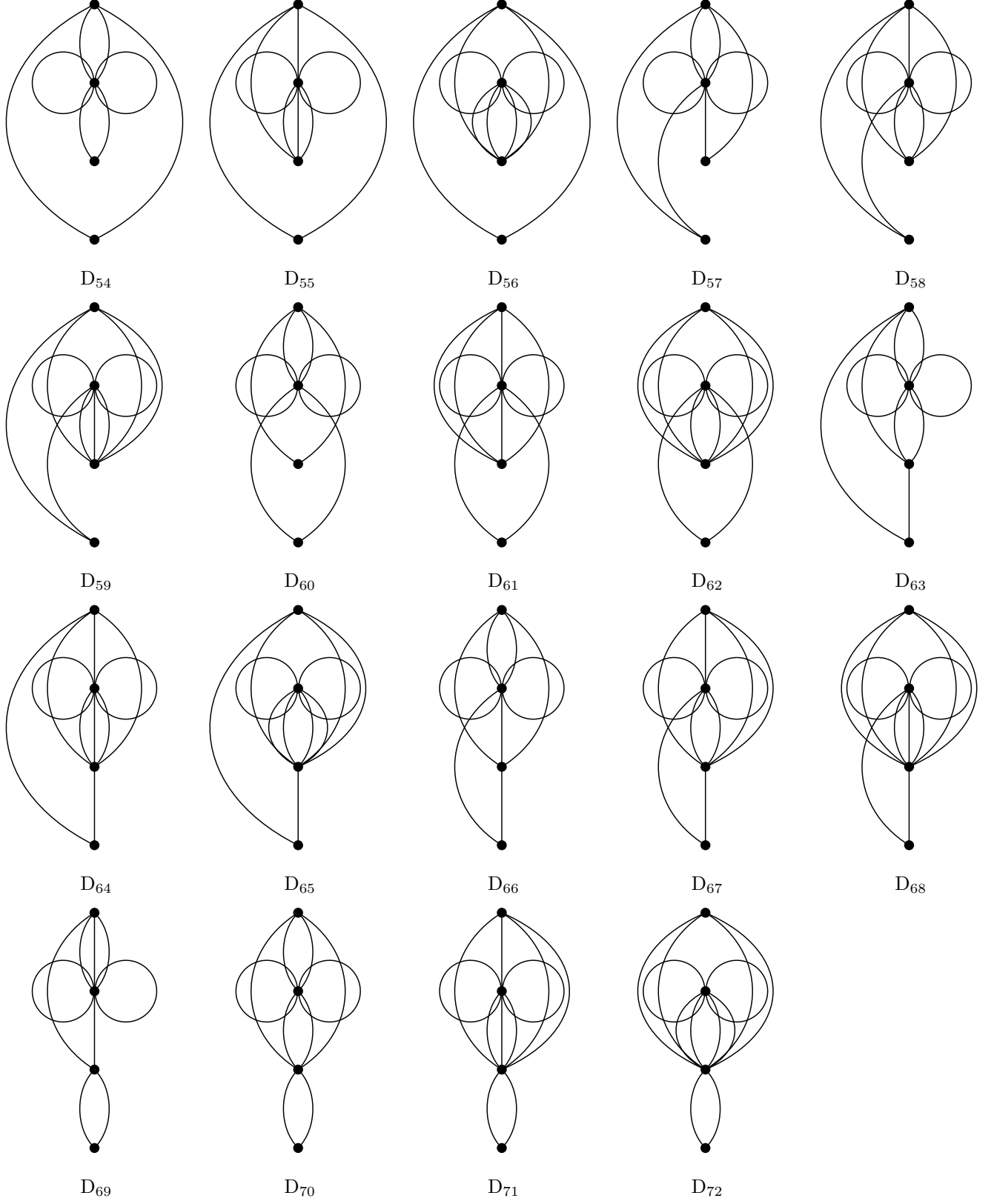


FIG. 5. 2-loop renormalized 4-vertex diagrams.

Since  $v_{pq}^F(t)$  is just a number, we are interested in evaluating the SQ operator  $e^{+iH_0t/\hbar}p^\dagger q e^{-iH_0t/\hbar}$ . We will start by inserting identity in this expression,

$$e^{+iH_0t/\hbar}p^\dagger q e^{-iH_0t/\hbar} = e^{+iH_0t/\hbar}p^\dagger e^{-iH_0t/\hbar} e^{+iH_0t/\hbar} q e^{-iH_0t/\hbar}. \quad (66)$$

The time-dependent creation and annihilation operators are defined as,

$$p^\dagger(t) = e^{+iH_0t/\hbar}p^\dagger e^{-iH_0t/\hbar} \quad (67)$$

$$q(t) = e^{+iH_0t/\hbar}q e^{-iH_0t/\hbar}. \quad (68)$$

Using BCH expansion,

$$q(t) = q + \frac{it}{\hbar}[q, H_0] + \frac{1}{2!}\left(\frac{it}{\hbar}\right)^2 [[q, H_0], H_0] + \dots \quad (69)$$

Using the results from Eq. (A15), derived in Appendix A,

$$[p, q^\dagger r] = \delta_{pq}r \quad (70)$$

Therefore,

$$[q, H_0] = \sum_{p_1 q_1} h_{p_1 q_1} [q, p_1^\dagger, q_1] \quad (71)$$

$$= \sum_{p_1 q_1} h_{p_1 q_1} \delta_{qp_1} q_1 \quad (72)$$

$$= \sum_{q_1} h_{qq_1} q_1. \quad (73)$$

Hence, we have the general result,

$$[q, H_0] = \sum_{q_1} h_{qq_1} q_1. \quad (74)$$

Similarly,

$$[[q, H_0], H_0] = \sum_{q_1} h_{qq_1} [q_1, H_0] \quad (75)$$

$$= \sum_{q_1 q_2} h_{qq_1} h_{q_1 q_2} q_2 \quad (76)$$

We note that the above expression can be written in terms of the matrix product

$$\sum_{q_1} h_{qq_1} h_{q_1 q_2} = [\mathbf{h}\mathbf{h}]_{qq_2} = [\mathbf{h}^2]_{qq_2} \quad (77)$$

Therefore, for m-terms expansion,

$$[[q, H_0], \dots, \text{m-terms}, H_0] = \sum_{q_1 q_2 \dots q_m} h_{qq_1} h_{q_1 q_2} h_{q_2 q_3} \dots h_{q_{m-1} q_m} q_m \quad (78)$$

$$= \sum_{q_m} [\mathbf{h}^m]_{qq_m} q_m. \quad (79)$$

Since  $q_m$  is just a summation index, we can rewrite the expression as,

$$[[q, H_0], \dots, \text{m-terms}, H_0] = \sum_{q_1} [\mathbf{h}^m]_{qq_1} q_1. \quad (80)$$

Substituting the above expression in the BCH expansion,

$$q(t) = q + \frac{it}{\hbar} \sum_{q_1} h_{qq_1} q_1 + \frac{1}{2!} \left(\frac{it}{\hbar}\right)^2 \sum_{q_1} [\mathbf{h}^2]_{qq_1} q_1 + \frac{1}{k!} \left(\frac{it}{\hbar}\right)^k \sum_{q_1} [\mathbf{h}^k]_{qq_1} q_1 \dots \quad (81)$$

Combining all the  $\mathbf{h}$ -terms

$$q(t) = q + \sum_{q_1} \left[ \frac{it}{\hbar} h_{qq_1} q_1 + \frac{1}{2!} \left( \frac{it}{\hbar} \right)^2 [\mathbf{h}^2]_{qq_1} + \frac{1}{k!} \left( \frac{it}{\hbar} \right)^k [\mathbf{h}^k]_{qq_1} \dots \right] q_1 \quad (82)$$

Expressing the first term  $q$  in terms of  $q_1$  using Kronecker delta,

$$q = \sum_{q_1} \delta_{qq_1} q_1 \quad (83)$$

we get,

$$q(t) = \sum_{q_1} \left[ \delta_{qq_1} + \frac{it}{\hbar} h_{qq_1} q_1 + \frac{1}{2!} \left( \frac{it}{\hbar} \right)^2 [\mathbf{h}^2]_{qq_1} + \frac{1}{k!} \left( \frac{it}{\hbar} \right)^k [\mathbf{h}^k]_{qq_1} \dots \right] q_1. \quad (84)$$

We recognize that the  $\delta$  in the above expression is the element of the identity matrix  $\mathbf{I}$ .

$$q(t) = \sum_{q_1} \left[ I_{qq_1} + \frac{it}{\hbar} h_{qq_1} q_1 + \frac{1}{2!} \left( \frac{it}{\hbar} \right)^2 [\mathbf{h}^2]_{qq_1} + \frac{1}{k!} \left( \frac{it}{\hbar} \right)^k [\mathbf{h}^k]_{qq_1} \dots \right] q_1 \quad (85)$$

We define matrix  $\tilde{\mathbf{h}}(t)$  as,

$$\tilde{\mathbf{h}}_A(t) = \frac{it}{\hbar} \mathbf{h}. \quad (86)$$

The subscript  $A$  is to remind us that it is an anti-hermitian matrix

$$\tilde{\mathbf{h}}_A^\dagger(t) = -\tilde{\mathbf{h}}_A(t). \quad (87)$$

Using the above definition, the sum in the square brackets can be written in terms of matrix exponentiation,

$$\sum_{k=0}^{\infty} \frac{1}{k!} \tilde{\mathbf{h}}_A^k(t) = e^{\tilde{\mathbf{h}}_A(t)} \quad (88)$$

where,

$$\tilde{\mathbf{h}}_A^0 = \mathbf{I} \quad (89)$$

and  $\mathbf{I}$  is identity matrix (and not scalar 1). Therefore, the time-development of  $q$  is given by,

$$q(t) = \sum_{q_1} [e^{\tilde{\mathbf{h}}_A(t)}]_{qq_1} q_1. \quad (90)$$

Similarly, the time-development of  $p^\dagger$  is given by,

$$p^\dagger(t) = \sum_{p_1} [e^{-\tilde{\mathbf{h}}_A(t)}]_{pp_1} p_1^\dagger. \quad (91)$$

Therefore,

$$e^{+iH_0 t/\hbar} V_F(t) e^{-iH_0 t/\hbar} = \sum_{pq} v_{pq}^F(t) p^\dagger(t) q(t) \quad (92)$$

$$= \sum_{pq p_1 q_1} v_{pq}^F(t) [e^{-\tilde{\mathbf{h}}_A(t)}]_{pp_1} [e^{\tilde{\mathbf{h}}_A(t)}]_{qq_1} p_1^\dagger q_1. \quad (93)$$

Using

$$[e^{-\tilde{\mathbf{h}}_A(t)}]^\dagger = e^{+\tilde{\mathbf{h}}_A(t)} \quad (94)$$

$$e^{+iH_0t/\hbar}V_F(t)e^{-iH_0t/\hbar} = \sum_{pq p_1 q_1} [e^{+\tilde{\mathbf{h}}_A(t)}]_{p_1 p} v_{pq}^F(t) [e^{-\tilde{\mathbf{h}}_A(t)}]_{q_1 q} p_1^\dagger q_1 \quad (95)$$

which is equal to,

$$e^{+iH_0t/\hbar}V_F(t)e^{-iH_0t/\hbar} = \sum_{p_1 q_1} [e^{+\tilde{\mathbf{h}}_A(t)} \mathbf{v}^F(t) e^{-\tilde{\mathbf{h}}_A(t)}]_{p_1 q_1} p_1^\dagger q_1. \quad (96)$$

Comparing to Eq. 64, we get the expression for the  $A$  amplitudes

$$\mathbf{A}(t) = e^{+(it/\hbar)\mathbf{h}} \mathbf{v}^F(t) e^{-(it/\hbar)\mathbf{h}}. \quad (97)$$

### B. Evaluation of time-dependent amplitudes associated with bare 2-body vertex

In this section, we will evaluate the expression of the time-dependent amplitude  $B_{pq}(t)$  associated with the bare 2-body vertex. The equation that defines this amplitude is given by the following equation,

$$e^{+iH_0t/\hbar}W e^{-iH_0t/\hbar} = \sum_{pqrs} B_{pqrs}(t) p^\dagger q^\dagger sr \quad (98)$$

where the 2-body operator is defined as,

$$W = \sum_{pqrs} W_{pqrs} p^\dagger q^\dagger sr. \quad (99)$$

Using the insertion of identity method used in the previous section, we express the above equation in terms of time-dependent SQ operators

$$e^{+iH_0t/\hbar}W e^{-iH_0t/\hbar} = \sum_{pqrs} W_{pqrs} p^\dagger(t) q^\dagger(t) s(t) r(t). \quad (100)$$

Substituting the previously derived expression for time-dependent SQ

$$p^\dagger(t) = \sum_{p_1} [e^{-(it/\hbar)\mathbf{h}}]_{p p_1} p_1^\dagger = \sum_{p_1} [e^{+(it/\hbar)\mathbf{h}}]_{p_1 p} p_1^\dagger \quad (101)$$

$$s(t) = \sum_{s_1} [e^{+(it/\hbar)\mathbf{h}}]_{s s_1} s_1 = \sum_{s_1} [e^{-(it/\hbar)\mathbf{h}}]_{s_1 s} s_1 \quad (102)$$

we get,

$$e^{+iH_0t/\hbar}W e^{-iH_0t/\hbar} = \sum_{pqrs} W_{pqrs} p^\dagger(t) q^\dagger(t) s(t) r(t) \quad (103)$$

$$\begin{aligned} &= \sum_{p_1 q_1 r_1 s_1 pqrs} [e^{+(it/\hbar)\mathbf{h}}]_{p_1 p} [e^{+(it/\hbar)\mathbf{h}}]_{q_1 q} \\ &\quad \times W_{pqrs} [e^{-(it/\hbar)\mathbf{h}}]_{r_1 r} [e^{-(it/\hbar)\mathbf{h}}]_{s_1 s} \\ &\quad \times p_1^\dagger q_1^\dagger s_1 r_1. \end{aligned} \quad (104)$$

The above relationship implies the following expression for the  $B$ ,

$$B_{p_1 q_1 r_1 s_1} = \sum_{pqrs} [e^{+(it/\hbar)\mathbf{h}}]_{p_1 p} [e^{+(it/\hbar)\mathbf{h}}]_{q_1 q} W_{pqrs} [e^{-(it/\hbar)\mathbf{h}}]_{r_1 r} [e^{-(it/\hbar)\mathbf{h}}]_{s_1 s}. \quad (105)$$

## VII. RESULTS AND CONCLUSION

The main result from this work is the explicit expressions for the time-dependent transition amplitudes for generation of 2e-2h pair from 1e-1h pair for excited states propagating in time under the influence of external electromagnetic field. Up to second-order the time-dependent transition amplitude is given by the following expression,

$$I_F(t_f) = I_F^{(0)} t_f + \int_0^{t_f} dt_1 I_F^{(1)}(t_1) + \int_0^{t_f} dt_1 \int_0^{t_1} dt_2 I_F^{(2)}(t_1, t_2). \quad (106)$$

Because of the complexity of the equation, a brute-force approach for the calculation of this expression is computationally prohibitive. In this work, we showed that the expressions for  $I_F^{(n)}$  can be separated into a time-dependent component and time-independent components. We have derived the expression for the time-dependent components and we show that these quantities can be expressed in terms standard matrix-matrix tensor-tensor contraction terms. The extraction of the time-independent components from the time-propagation equation presents a significant computational advantage because the time-independent component can be evaluated at the start of the calculation and can be reused during the course of the time-dependent calculation. This strategy dramatically reduces the computational complexity of for performing such calculations. We have also presented the explicit results from the calculation of the time-dependent quantities (denoted by  $\eta$ ) in terms of the diagrammatic representation.

One of the key results from this work is the general treatment of electron correlation in the derived result. The inclusion of electron-electron correlation for the excited state is done by the operator  $\Omega$  in Eq. 8. In the derivation presented here, we have not imposed any specific form for the electron-correlation operator. As a consequence, the set of diagrams presented in Fig. 2 and 3, is the complete set of diagrams associated any form of  $\Omega$ . If  $\Omega$  is chosen to be an N-body operator like the full-CI or coupled-cluster wave functions, all the diagrams presented in Fig. 4 and 5 will contribute to the transition amplitudes. However, if  $\Omega$  is chosen to be a 2-body operator only a subset of those diagrams will contribute.

The complexity and computational cost of the evaluation of the diagrams increase with increasing number of vertices. Out of the 3-vertex, 4-vertex, and 5-vertex diagrams, the 5-vertex diagrams are most expensive to calculate. In this derivation, we have shown that a subset of the 5-vertex diagrams can be factored into pre-existing 3- and 4-vertex diagrams. We also present a renormalization scheme for the 5-vertex diagrams by expressing them as 1-loop and 2-loop contracted effective 4-vertex diagrams. The renormalization method and the factorization of diagrams utilizes reusability of pre-computed results and contributes in reducing the overall cost of the calculations. We envision that the developed method can be used for the investigation of time-dependent carrier multiplicity in both semiconductor and organic photoactive systems.

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## APPENDIX

### Appendix A: Commutator identities

The commutator and anticommutator is defined as,

$$[A, B] = AB - BA \quad (\text{A1})$$

$$[A, B]_+ = AB + BA. \quad (\text{A2})$$

Note that,

$$[B, A] = -[A, B] \quad (\text{A3})$$

$$[B, A]_+ = [A, B]_+. \quad (\text{A4})$$

The fermionic second-quantized operators satisfy the following anticommutation relationships,

$$[p^\dagger, q^\dagger]_+ = 0 \quad (\text{A5})$$

$$[p, q]_+ = 0 \quad (\text{A6})$$

$$[p^\dagger, q]_+ = \delta_{pq}. \quad (\text{A7})$$

This is a well-known identity commutator identity

$$[A, B_1 B_2] = B_1 [A, B_2] + [A, B_1] B_2 \quad (\text{A8})$$

$$[A_1 A_2, B] = A_1 [A_2, B] + [A_1, B] A_2. \quad (\text{A9})$$

The corresponding anticommutator identity is,

$$[A, B_1 B_2]_+ = [A, B_1] B_2 + B_1 [A, B_2]_+ \quad (\text{A10})$$

$$= [A, B_1]_+ B_2 - B_1 [A, B_2]. \quad (\text{A11})$$

The commutator can be written in terms of the anticommutator as well,

$$[A, B_1 B_2] = [A, B_1]_+ B_2 - B_1 [A, B_2]_+. \quad (\text{A12})$$

These relationship can be extended to a series of operators

$$[A, B_1 \dots B_N] = \sum_{k=1}^N B_1 \dots B_{k-1} [A, B_k] B_{k+1} \dots B_N \quad (\text{A13})$$

$$[A, B_1 \dots B_N]_+ = \sum_{k=1}^N (-1)^{k-1} B_1 \dots B_{k-1} [A, B_k]_+ B_{k+1} \dots B_N. \quad (\text{A14})$$

The commutation of a single SQ operator with 1-body operator generates a single SQ operator,

$$[p^\dagger, q^\dagger r] = -\delta_{pr} q^\dagger \quad (\text{A15})$$

$$[p, q^\dagger r] = \delta_{pq} r. \quad (\text{A16})$$

The commutator with two one-body operators generate a sum of two one-body operators,

$$[p^\dagger q, r^\dagger s] = \delta_{qr} p^\dagger s - \delta_{ps} r^\dagger q. \quad (\text{A17})$$

The commutator of a one and two-body operator generates a sum of two-body operators

$$[p^\dagger q, r^\dagger s m^\dagger n] = \delta_{qr} p^\dagger s m^\dagger n - \delta_{ps} r^\dagger q m^\dagger n + \delta_{qm} r^\dagger s p^\dagger n - \delta_{pn} r^\dagger s m^\dagger q. \quad (\text{A18})$$

The general expression for the above results can be summarized as follows. The commutator of two 1-body operators is another 1-body operator,

$$[p_1^\dagger q_1, p_2^\dagger q_2] = \lambda_{pq\dots p_2 q_2} p_1^\dagger q \quad (\text{A19})$$

$$\lambda = \delta_{q_1 p_2} \delta_{p p_1} \delta_{q q_2} - \delta_{p_1 q_2} \delta_{p p_2} \delta_{q q_1}. \quad (\text{A20})$$

## Appendix B: Commutation with 1-body operator

$$A = \sum_{p_1 q_1} A_{p_1 q_1} p_1^\dagger q_1 \quad (\text{B1})$$

$$B = \sum_{p_2 q_2} B_{p_2 q_2} p_2^\dagger q_2 \quad (\text{B2})$$

$$[A, B] = \left[ \sum_{p_1 q_1} A_{p_1 q_1} p_1^\dagger q_1, B \right] \quad (\text{B3})$$

$$= \sum_{p_1 q_1} A_{p_1 q_1} [p_1^\dagger q_1, B] \quad (\text{B4})$$

$$= \sum_{p_1 q_1 p_2 q_2} A_{p_1 q_1} B_{p_2 q_2} [p_1^\dagger q_1, p_2^\dagger q_2] \quad (\text{B5})$$

Using

$$[p_1^\dagger q_1, p_2^\dagger q_2] = \delta_{q_1 p_2} p_1^\dagger q_2 - \delta_{p_1 q_2} p_2^\dagger q_1 \quad (\text{B6})$$



We get,

$$[A, B] = \sum_{p_1 q_1 p_2 q_2} A_{p_1 q_1} B_{p_2 q_2} [p_1^\dagger q_1, p_2^\dagger q_2] \quad (\text{B7})$$

$$= \sum_{p_1 q_1 p_2 q_2} A_{p_1 q_1} B_{p_2 q_2} (\delta_{q_1 p_2} p_1^\dagger q_2 - \delta_{p_1 q_2} p_2^\dagger q_1) \quad (\text{B8})$$

$$= \sum_{p_1 q_1 p_2 q_2} A_{p_1 q_1} B_{p_2 q_2} \delta_{q_1 p_2} p_1^\dagger q_2 - \sum_{p_1 q_1 p_2 q_2} A_{p_1 q_1} B_{p_2 q_2} \delta_{p_1 q_2} p_2^\dagger q_1 \quad (\text{B9})$$

$$= \sum_{p_1 q_2 t} A_{p_1 t} B_{t q_2} p_1^\dagger q_2 - \sum_{q_1 p_2 t} A_{t q_1} B_{p_2 t} p_2^\dagger q_1 \quad (\text{B10})$$

Using

$$\sum_t A_{p_1 t} B_{t q_2} = [\mathbf{A}\mathbf{B}]_{p_1 q_2} \quad (\text{B11})$$

$$\sum_t B_{p_2 t} A_{t q_1} = [\mathbf{B}\mathbf{A}]_{p_2 q_1} \quad (\text{B12})$$

We get,

$$[A, B] = \sum_{p_1 q_2} [\mathbf{A}\mathbf{B}]_{p_1 q_2} p_1^\dagger q_2 - \sum_{q_1 p_2 t} [\mathbf{B}\mathbf{A}]_{p_2 q_1} p_2^\dagger q_1 \quad (\text{B13})$$

Using general indices, we can write the above expression as,

$$[A, B] = \sum_{pq} C_{pq} p^\dagger q \quad (\text{B14})$$

$$\mathbf{C} = [\mathbf{A}, \mathbf{B}]. \quad (\text{B15})$$

Therefore, formally we can write that commutator of two 1-body operators is another 1-body operator,

$$[\hat{A}, \hat{B}] = \hat{C}. \quad (\text{B16})$$

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